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Study of Electronic Structure and Tunneling-Transport Properties of Novel Rare-Earth-Compound/Semiconductor Interfaces and Quantum Wells

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In this grant electronic structure and transport properties of several magnetic rare earth compounds such as Er and Gd pnictides were investigated by means of several first-principle and model techniques. Several other potentially important magnetic compounds such as MnAl, MnGa, and GaMnAs were also considered. All these materials can be grown epitaxially on GaAs or other conventional semiconductors thus forming magnetic heterostructures or nanocomposites. Our work provided solid theoretical background for a number of new experiments and significantly improved understanding of some recently discovered phenomena such as:

- Shubnikov-DeHaas oscillations in bulk ErAs
- Spin-dependent resonant tunneling in GaAs/ErAs double-barrier heterostructures
- Colossal magnetoresistance in GaAs/ErAs nanocomposites

We have also resolved several materials science issues such as:

- Schottky barrier formation at GaAs/ErAs interfaces
- Magnetic anisotropy of MnAl and MnGa
- Growth of self-assembled MnAl quantum dots on GaAs

Our work identifies several important applications related to spin-dependent transport in semiconductor-based magnetic heterostructures and nanocomposites.

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Abstract

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1 Introduction

This grant was concerned with comprehensive studies of electronic structure and related properties of rare-earth pnictides (e. g. ErAs) and their interfaces with conventional semiconductors (e. g. GaAs). We have also investigated spin-dependent quantum transport in ErAs/GaAs-based heterostructures and nanocomposites. In addition, we performed electronic structure calculations of other potentially important magnetic materials such as MnAl and MnGa and initiated MOCVD growth of MnAl quantum dots on GaAs.

Our work was initially aimed at the studies of ErAs/GaAs-based heterointerfaces and double barrier structures. During the course of our research several new experimental results were obtained concerning magnetotransport in ErAs/GaAs nanocomposites and in GaAs/GaMnAs resonant tunneling diodes. Therefore, we significantly expanded the scope of our studies by including these systems into consideration. We also studied some other potentially important magnetoelectronic materials such as MnAl and MnGa and initiated MOCVD growth of GaAs/MnAl nanocomposites.

The growing interest in these systems originates from the technological drive to integrate dense magnetic storage with high-speed electronics, and to create ultrafast and non-volatile memories. The idea of controlling and manipulating carriers' spins can be utilized in a new rapidly growing field of quantum computations. We believe that our work will facilitate the development of novel quantum devices, which merge magnetism with semiconductor technologies.

2 Research Objectives

The research objectives of this project were clearly stated in the proposal. During the course of this grant we formulated our research goals in much broader sence:

- Search, feasibility studies, and modeling of new magnetic nanostructures and heterostructures based on RE-V/GaAs and GaMnAs/GaAs materials systems.
- Equilibrium interface geometry, Schottky barriers, and band offsets for several ErAs/GaAs technologically important interfaces of different orientations.
- First-principle calculation of current-voltage characteristics of working RE-V/GaAs-based resonant tunneling diodes (RTDs).
- Theory of giant hopping magnetoresistance in ErAs/GaAs nanocomposites.
- First-principle calculation of relativistic (involving spin-orbit coupling) electronic band structure and of electronic, magnetic, and total-energy properties of bulk MnAl and MnGa
- An attempt to grow τ-phase MnAl on GaAs substrates using MOCVD.

3 Results Overview

In the course of our work we initiated and completed several projects in accordance with research objectives formulated above. Here we present a brief overview of these projects and their results.

3.1 Electronic Structure of bulk Rare Earth Pnictides

The electronic structure of bulk rare-earth compounds such as ErAs, ErN, ErP, GdAs, GdP, and GdN has been investigated quantitatively in details. The results of first-principles linear-muffin-tin orbital (LMTO) calculations are in very good agreement with available experimental data. We predicted that the arsenides and phosphides are semimetals while nitrides are semiconductors with band gaps tunable by a magnetic field. With the spin-orbit interaction taken into account we were able to analyze and identify all the peculiarities of the Shubnikov-de Haas spectrum of the ErAs layers buried in GaAs in excellent agreement with experiment. These results were obtained using the linear-muffin-tin orbital method in the atomic sphere approximation and treating the localized 4f electrons as atomic boundary insensitive core-like electrons.

We conclude that this treatment of the 4f electrons is quite satisfactory for most purposes not directly involving the 4f states. It was found to provide lattice constants in good agreement with experiment showing that the 4f's are not significantly involved in the bonding in these materials and that their charge density is well represented. It accounts well for the major features of the electronic structure and magnetic properties of this family of materials. In particular, it leads to a semimetallic band structure (bordering on a transition to semiconductors for the nitrides) while a straightforward band treatment of the 4f states does not. Furthermore, the maximum electron spin alignment of the localized 4f electrons provides a natural explanation for the existence of well established local moments which in turn induces exchange splittings in the valence bands in the presence of an external magnetic field or in the low temperature (anti)ferromagnetic phases. This induced itinerant magnetism although small leads to observable effects in magnetotransport. The persistence of such moments also explains the small energy difference between the non-magnetic and magnetic phases (because the latter is almost entirely due to the small induced moments) which is consistent with the small Néel temperatures observed in ErAs and ErP. Furthermore, we showed that interaction effects between the actual 4f multiplets and the bands in the neighborhood of the Fermi level are expected to be small. Although we have in the present work not attempted to directly determine the actual positions of the 4f derived bands with respect to the bands, we anticipate that this can be achieved by means of Slater's transition state rule and expect them to be similar to those in the corresponding pure rare-earth metals.

Our calculations provide several predictions of presently unknown properties of these materials. These include the bulk moduli and induced magnetic moments as well as band structure dispersions, band gaps, effective masses and exchange splittings. For ErAs, the only material in this family which has been studied experimentally to some extent, we obtained good agreement for most of the band structure related properties as determined from magnetotransport measurements. This is the case for the overall topology of the Fermi surface, the exchange splittings and the effective masses. We reviewed our previous detailed study [1] of the magnetotransport properties in $Er_xSc_{1-x}As$ and augmented it in view of recent additional measurements. We concluded that inclusion of the spin-orbit coupling is likely to explain the remaining discrepancies. The only exception to good agreement is the overall size of the Fermi surface, as determined by Shubnikov-de Haas oscillations and the carrier concentration obtained from Hall effect measurements. In fact, we found that our LDA calculations

give an overestimate of the Fermi surface volume by about a factor of three. This discrepancy, however, could be eliminated by a simple rigid band shift of the Er 5d band by only 0.4 eV. A shift of this magnitude can be expected to arise from quasiparticle self-energy corrections of the same type that affect band gaps in semiconductors. This was shown by explicitly estimating such corrections within a simple model. While, unfortunately, this model is too crude to allow an accurate determination, it does yield roughly the correct shift for ErAs. Furthermore, since the gap corrections were predicted by the simple model to be rather constant throughout the series of materials investigated, we can with some confidence expect corrections for the other materials of roughly the same magnitude as for ErAs. This allows us, for example, to predict that ErN and GdN are narrow gap semiconductors in their paramagnetic phases.

The results of these studies were presented at several conferences and published in Physical Review B [1, 2, 3]. This work was performed in collaboration with W.R.L. Lambrecht and B. Segall from Case Western Reserve University.

3.2 Electronic Structure and Equilibrium Geometry of ErAs/GaAs Schottky Barriers

In the second year of the project, we completed studies of the ErAs/GaAs Schottky barriers. The electronic structure and total energies of different models of ErAs/GaAs interfaces have been calculated by means of the full-potential (FP) LMTO method. Our study addressed the extensive set of experimental data obtained by Palmstrøm et al. [4] on this system and is important for a full understanding of the RE-V/GaAs systems in general. We started by doing extensive calculations of the (001) interface. FP-LMTO calculations were carried our to optimize the interface structure for two models suggested by experiment: the chain model and the shadow model. In the first, the GaAs is terminated in Ga, in the second it is terminated in As. One can alternatively think of the first model as resulting from a conversion of the top As layer of GaAs into the first ErAs layer. Subsequently, we analyzed their electronic structure by calculating partial densities of electronic states, charge densities, etc. These time consuming calculations finally led to the main conclusion that the interface bonding is weak. For example, for the chain model, the interface ErAs layer is found to debond from the GaAs resulting in a 60% increase in the interplanar distance between Ga terminating layer and the first ErAs layer. The charge densities showed dangling bond character. Also, it was found that the Fermi level of the models was pinned by interface states resembling surface dangling bond states. Hence, we decided it would be useful to compare the interface partial density of states with that of the surfaces of the individual components, in particular with the GaAs surfaces. These GaAs calculations were carried out for the same thin slab models as occuring in the ErAs/GaAs interface model. Partial densities of states of both interface and surface were obtained using the atomic sphere approximation LMTO version but using the structure obtained from FP-LMTO. The comparison showed very clearly that the interface states are similar to the corresponding free surface states of our GaAs surface models. This constitutes an important insight which provides a simple way for speculating about the interfaces of other crystallographic orientation. This led to some first insights into the reason for the orientation dependence of the Schottky barrier height.

In summary, we predicted that GaAs surface at the lowest energy GaAs/ErAs

interface is terminated with Ga layer. This interface is a classical example of Bardin model of a Schottky barrier when the Schottky barrier height is determined by the surface state of GaAs. Our value of the Schottky barrier height for the Ga terminated GaAs/ErAs interface is in fair agreement with the experiment (C.J. Palmstrom et al. [4]) The results of this work were presented at the AFOSR program review in Santa Barbara in August 97 and published in Solid State Communications [5]. They were also presented at the Fall MRS meeting and APS March Meeting [6] and a paper on these results was published in the MRS conference proceedings [7].

3.3 Electronic Structure of Ferromagnetic Materials Lattice-Matched to GaAs

The electronic structure of technologically important bulk Mn alloys such as MnAl, and MnGa has been investigated quantitatively. We have performed first-principle calculations of equilibrium lattice constants, band structures, densities of states and magnetocrystalline anisotropy energy for bulk MnAl and MnGa. The linear-muffin-tin-orbital (LMTO) method has been used within the framework of the local spin density approximation (LSDA). Both the atomic sphere approximation (ASA) and the full-potential (FP) versions of the LMTO method were employed.

Calculations of the equilibrium structures were performed both for paramagnetic and ferromagnetic phases of MnAl and MnGa. The results of these calculations indicate that the large tetragonal distortion of the crystal structure is caused by the spin polarization of the electronic subsystem. The magnetocrystalline anisotropy energy per unit cell for MnAl and MnGa is shown to be 0.244 meV and 0.422 meV respectively. This is in good agreement with previous calculations and some experimental data [8, 9, 10]. Magnetic moments, density of states and dependence of magnetocrystalline anisotropy energy on the lattice constant ration c/a are also found to be in good agreement with previous results. All results can be briefly summarized as follows.

3.3.1 MnAl

In Table 1 we summarize all of the obtained results. The calculated lattice parameters are a=2.699 Å, c=3.319 Å and a=2.804 Å, c = 2.972Å from spin-polarized and non-spin-polarized calculations respectively. The energy difference between non-spin-polarized and spin polarized states is 85 meV/atom. The non-spin-polarized calculated

Table 1: Equilibrium lattice constants and magnetic anisotropy energy (MAE)

Compound	a (Å), SP.	a (Å), non-SP.	c/a SP	c/a non-SP	MAE (meV/unit cell)
MnAl	2.699	2.804	1.23	1.06	0.244
MnGa	2.540	2.752	1.46	1.11	0.422

value of lattice parameter a is closer to the experimental one. In fact, the difference between non-spin-polarized calculated and the experimental value is within the ordinary limits given by all other similar calculations. However the non-spin-polarized calculations fail to predict the correct value for the crystal deformation parameter, c/a. This value is more accurately predicted by spin-polarized calculations. This fact clearly indicates that the deformation of the crystal is caused mainly by its magnetization.

The results of spin-polarized band structure calculations for MnAl showed that there is no band gap at the Fermi level and that a large exchange splitting of about 2 eV exists between Mn 3d states with opposite spins. The non-spin polarized density of states (DOS) for MnAl was also calculated. The DOS of Mn has a sharp maximum at the Fermi level, which leads us to expect that MnAl is ferromagnetic.

The spin-polarized DOS for MnAl are found to have the following features. The long tail in the range between -10 and -5 eV is mainly due to Al s states and Mn s states. The Al p states give a small contribution to the density of states, in the region adjacent to -5 eV while Mn d states are spread all over the calculated range and have the largest contribution in the range between -2 and 2 eV, where the total density of states almost coincides with Mn d-DOS. The calculated magnetic moments for Mn and Al are -2.192 μ_B and 0.042 μ_B respectively. These values are slightly higher than the experimental ones [11], but the stoichiometry of the measured samples differs from the ideal one, for which all calculations are made.

The results of magnetocrystalline anisotropy energy calculations for both MnAl and MnGa are shown in Table 1. At equilibrium, the MAE for MnAl is 0.244 meV per unit cell. This value is in good agreement with previous calculations and corresponds to $\hat{n}$ in the [100] direction of the tetragonally distorted reduced crystal structure of MnAl or MnGa. This means that in bulk MnAl, the axis of easy magnetization lies in the c-plane rather than in x, y-plane. Within the accuracy of our calculations it is impossible to predict the exact direction of the easy magnetization axis in the c-plane. The calculated value of the MAE, leads to the value $1.4\times\ 10^6\ J/m^3$ for the magnetic anisotropy constant K_u which is close to the measured value as well. The dependence of MAE upon the deformation c/a, indicates that the easy magnetization axis turns from the c-plane to the x, y-plane whenever the deformation c/a is smaller than 1 or larger than 1.6.

3.3.2 MnGa

For MnGa we have almost the same picture with the exception that the obtained MAE, 0.422 meV per unit cell, is almost two times larger. This leads to a magnetic anisotropy constant K_u of $2.6\times10^6 J/m^3$. Unfortunately, we are not aware of any experimental data for the magnetic anisotropy constant of this material. The dependence of MAE on the c/a also differs considerably from that obtained for MnAl. It is shown that the easy magnetization axis turns from the c-plane to the x, y-plane only when c/a is below 1. Another interesting fact is that the deformation in the equilibrium structure is also much greater than that of MnAl. The difference between spin polarized calculated and non-spin polarized calculated equilibrium c/a for MnGa is about two times larger than that in MnAl. This fact and the fact that the MAE for MnGa is also about two times larger than that of MnAl is a clear indication that the tetragonal deformation and the magnetic anisotropy are closely related to each other.

The results of the equilibrium structure calculations indicate that while non-spin-polarized calculations give accurate value of the lattice constant a they fail to predict the correct value of the deformation parameter c/a. Again, this value is more accurately predicted by spin-polarized calculations. The calculated equilibrium lattice constants and magnetic moments are shown in Table 1.

The results of these studies were presented at MRS meeting and will be published in Materials Research Society Proceedings [12].

3.4 Spin-Dependent Resonant Tunneling in ErAs/GaAs Resonant Tunneling Diodes

In the course of our work a novel effect was discovered in S. J. Allen's group, namely spin-dependent resonant tunneling in GaAs/AlAs/ErAs/AlAs/GaAs structures [13]. The experiments were carried out on the RTD structures consisting of semimetal ErAs quantum wells and AlAs barriers sandwiched between the n^+ doped GaAs substrate and GaAs capping layers. The most extensive and the ones we focused on were obtained for the (311) orientation of the films. The measurements of differential conductance indicated the presence of two different resonant channels. One peak splits in a magnetic field perpendicular to the layers while another showes no observable splitting for either direction of the field, it is almost unresolved in zero or perpendicular field and is induced and enhanced by a field parallel to the field. Our work provided the theoretical understanding of this effect in terms of total (spin + orbital) angular momentum conservation combined with $k_{||}$-conservation. It also established that the tunneling took place through hole states in ErAs and that these states are spin-split as well as the electron states. It provided a detailed account of the experiments, the magnetic field orientation dependence and the switching on of a second resonant channel in magnetic fields parallel to the interfaces.

To summarize this explanation, we note that for the wave vector along (311) direction in semimetal ErAs unoccupied electron states are more than 1.5 eV above the Fermi level and there is a gap of about 1 eV between the unoccupied valence and conduction states. [2]. Therefore, the only states available for resonant tunneling are the ErAs confined hole states, since electrons tunneling from a vicinity of the Γ point of n^+ GaAs in the direction (311) must have their lateral momentum $k_{||} \simeq 0$ conserved. In other words, the GaAs/ErAs RTD is an example of a system with Zener-like interband tunneling. For this system the potential across the junction is a barrier for electrons and, at the same time, it is a confining potential for holes. Since the structure of the valence band of ErAs is similar to that of GaAs one can expect a significant role of spin-orbit coupling and symmetry effects in the resonant tunneling [3, 1]. The spin-orbit interaction couples the spin direction (determined by the magnetic field) to the direction of the orbital angular momentum of holes (determined by the normal to the interface). That is why the angular momentum conservation plays a crucial role for the interpretation of the experiment.

Namely, with the magnetic field absent or perpendicular to the layers, the projection of angular momentum onto the interface normal M_J is a good quantum number that must be conserved. The tunneling of s-like electrons with $|M_J| = 1/2$ from GaAs conduction band minimum into the heavy hole states with $|M_J| = 3/2$ (second channel) will be forbidden by symmetry. This explains why in that case the second channel is

almost unresolved while the first channel (corresponding to the tunneling into the light hole states with $|M_J = |1/2)$ is quite pronounced. For in-plane fields, the states with $|M_J| = 1/2$ and $|M_J| = 3/2$ are mixed and the second channel becomes available for tunneling.

The work was later further pursued to provide a fully quantitative account of the spin-dependent transmission coefficient within a model description. We believe that the developed theory will have wide range of applications in novel magneto-electronics. It can be easily generalized for studying spin-dependent tunneling through three-dimensional magnetic quantum dots. The interband spin-dependent resonant tunneling is a new and exciting phenomenon which may lead to a fabrication of novel semiconductor devices such as resonant tunneling spin-valve diodes.

The results of this work were presented at the APS and MRS meetings, International Conference on Physics of Semiconductor Interfaces (ICFSI) in Cardiff, Wales, 1997, and at the International Semiconductor Device Research Symposium (ISDRS) in Charlottesville, VA, 1997. The articles were published in Physical Review B [1], Applied Surface Science [14], and ISDRS Proceedings [15].

3.5 Spin-Dependent Resonant Tunneling in GaAs/GaMnAs Double Barrier Heterostructures

In this part of the project we have performed calculations of the transmission coefficients, tunneling current-voltage characteristics, and spin polarization of hypothetical p-GaAs/AlAs/$Ga_xMn_{1-x}As$/AlAs/p-GaAs RTDs. Our approach was based on the transfer-matrix technique using $\mathbf{k} \cdot \mathbf{p}$ perturbation theory with exchange splitting effects taken into account. Parameters of the exchange field were determined from the results of first-principle LMTO calculations. As a first example, we considered the transmission coefficient of the RTD with 10 Å-wide AlAs barriers and a 50 Å-wide $Ga_{0.99}Mn_{0.01}As$ quantum well. The total transmission coefficients of the structure in question at zero bias for zero and saturated magnetization in the quantum well, which is perpendicular to the layers were obtained. Electronic states in the quantum well define a very sharp structure (i. e. the sequence of peaks an valleys) of transmission coefficients. A very pronounced Zeeman splitting of the heavy hole (HH) channels and the first light hole channel (LH1) can be detected. As one can expect Zeeman splitting of the HH ($m_j = 3/2$) channels is much larger than that of the LH ($m_j = 1/2$) channels. Also, mixing of the LH and HH channels is quite substantial at $k_{||} \neq 0$. In case of in-plane magnetization only LH channels are split.

This quite pronounced structure of the transmission coefficient (including Zeeman splittings) manifests itself in the $I - V$ characteristics. We have calculated $I - V$ characteristics of three RTDs, for three different doping levels of the p-type emitter. Zeeman splittings of the resonant channels can be clearly seen in the current-voltage characteristics of the first RTD with E_F=-0.005 eV. The impact of magnetization is still quite dramatic for another RTD with a higher doping level (E_F=-0.015 eV). For the third RTD, however, E_F=-0.054 eV and the magnetization induced effects are rather modest. They can be revealed only in the differential conductance dI/dV versus voltage characteristics.

There is no surprise that both high values of the Fermi level and complex character of the band structure of the emitter make it difficult to observe a distinct RT structure

and, particularly, magnetization controlled RT. On the other hand, the RTDs with the low concentration of holes in the emitter, for which the effects of magnetization are quite significant, will have relatively low current densities. One of the possible alternatives providing for the observation of stronger magnetization controlled effects would be fabrication of structures, utilizing interband spin-dependent RT.

The results of this work where presented at the PCSI conference, Conference on Physics and Chemistry of Semiconductor Interfaces, Salt Lake City, UT, Symposium on Spin-Electronics, Halle, Germany, and Gordon Conference on Magnetic Nanostructures, Ventura, CA. They will be published in July/August issue of Journal of Vacuum Science and Technology A&B [16].

3.6 Giant Hopping Magnetoresistance in ErAs/GaAs Nanocomposites

We developed theory of another striking phenomenon discovered by S. J. Allen's group - Giant Magnetoresistance (GMR) of ErAs Quantum Dots immersed in GaAs (D. Schmidt, S. J. Allen et al.). This effect is explained in terms of hopping of bound magnetic polarons (BMP). A theory of bound magnetic polaron (BMP) hopping, driven by thermodynamic fluctuations of the local magnetization, has been developed. It is based on a two-site model of BMP. The BMP hopping probability rate was calculated in the framework of the "Golden Rule" approach by means of the Ginzburg-Landau effective Hamiltonian method. The particular mechanism responsible for GMR was identified as the electron hopping in a system in which a carrier strongly interacts with the localized magnetic moments of either transition-metal atoms (e. g. in dilute magnetic semiconductors) or of rare-earth atoms (e. g. in ErAs/GaAs nanostructures). In these systems, an electron or hole trapped by any kind of attractive potential of a defect, quantum dot, etc., can form a "cloud" of aligned spins of the surrounding magnetic atoms. Creation of such a complex (referred to as bound magnetic polaron) will further lower the free energy of the system by a quantity W_p called a polaron shift. The mechanism of the elementary hopping event takes into account thermodynamic fluctuations of the local magnetizations that control the elementary hopping act. Indeed, since the electron energy levels at both sites follow the fluctuations of local magnetic order parameters, it is likely that the levels at the occupied and empty sites will move in opposite directions thus getting into resonance. For this to occur, the occupied site should spontaneously decrease its local magnetization while the empty one should increase it. The electron can then tunnel from one site to another resonantly. This process somewhat resembles the multiphonon mechanism of small-polaron hopping [17]. It requires an activation energy $W_p/2$ [18] which is four times smaller compare to that of the so-called "static" mechanism considered by other authors [19, 20]. The giant negative magnetoresistance observed in dilute magnetic semiconductors was properly attributed by many authors ([19] and references therein) to the BMP phenomenon. Indeed, the application of a large magnetic field will quench magnetic polarons by reducing the magnetic part of their binding energy and therefore the activation energy of the hopping conductivity. However, the presence of a significant (up to 300%) positive magnetoresistance, which is typical for situations when the carriers are localized [19], remained unclear. We have shown that the latter is a signature of the fluctuation BMP hopping mechanism and ultimately reflects the fact that, in contrast to conventional

lattice polarons, the BMPs are described by a vector order parameter.

The theory explains the main features of hopping resistivity observed in a variety of experiments in dilute magnetic semiconductors and magnetic nanocomposites, namely: (a) the negative giant magnetoresistance the scale of which is governed by a magnetic polaron localization volume and (b) the low magnetic field positive magnetoresistance which usually precedes the negative magnetoresistance.

Recently we were able to explain the anisotropy of GMR in ErAs/GaAs nanocomposites (D. Schmidt, S. J. Allen et al.). The theory is based on the fact that the g-factor of heavy holes in ErAs is highly anisotropic and, therefore, the vector of Zeeman splitting is sensitive to the shape anisotropy of ErAs islands.

The results of this work were presented at the APS [21] and MRS meetings and published in MRS proceedings [22], Physical Review Letters [23], and Physical Review B [24].

3.7 MOCVD Growth of Ferromagnetic Quantum Dots on GaAs

In order to bring observed novel phenomena to room temperatures we initiated MOCVD growth of MnAl layers buried in GaAs [25].

The first stage was to explore how well Mn all by itself was deposited on the GaAs substrate. Substrate temperature, chamber deposition pressure, bubbler source flow rates, and bubbler temperature were varied to determine which of these parameters had a strong impact on the actual Mn deposition. SEM analysis was used to measure the presence and relative concentration of Mn on the surface. The basic conclusions are:

1. For substrate temperatures at or below 450 C, little or no Mn deposition occurs. This is most likely because the metalorganic molecules are not cracking apart into their constituent components (no free Mn as it is still bound in the molecule). Temperature analysis on InP, InGaAs, and GaAs deposition in previous research also showed that the 450-500 C temperature range was the minimum temperature needed to initiate deposition (at least in our MOCVD reactor in its current configuration).
2. Doubling the chamber deposition pressure from 20 Torr to 40 Torr did not measurably change the Mn deposition.
3. Increasing the bubbler temperature from 17 °C to 25 °C and 35 °C also did not appear to significantly alter the Mn deposition. However, since the transport lines were not also heated to 25 °C or 35 °C, the Mn vapor could easily have been condensing along the transport lines. Thus, no truly conclusive statements should be made about the effect of bubbler temperature until this can be studied more in the future.
4. As expected, the bubbler source flow rates had the most impact on actual Mn deposition.
5. Measurable and significant Mn deposition can be obtained at 550 °C on GaAs with MOCVD using the methylcyclopentadienylmanganese tricarbonyl. No information about whether oxygen is or is not present in the epilayers is available yet as oxygen appears to be below the detection threshold of our SEM.

The second stage was to deposit actual MnAl epilayers on GaAs substrates at 550 °C. This chemistry (between the aluminum and the manganese source) was completely unknown and unexplored as far as we were aware. The basic results are

1. We chose a relatively low aluminum flow rate as compared to manganese as aluminum is known to be quite reactive in CVD. This was immediately proved to be true, as the surfaces of the samples from the MnAl growth runs continued to change color after being removed from the chamber indicating the formation of Al oxides (the specimens grown with only Mn never showed such dramatic oxidation). So Al was certainly present and this was verified by SEM analysis which showed that the epilayers were 98% or more aluminum.
2. We proceeded to adjust the Al flow rates to try to lower the Al percentage. It became evident that this alone would not be sufficient to reach the target composition of approximately $Mn_{0.6}Al_{0.4}$.
3. The next major step we took was to lower the Al bubbler temperature from 17 °C to -10 °C. We could now grow $Mn_{0.3}Al_{0.7}$ layers (as determined by SEM analysis).
4. Using the Atomic Force Microscope (AFM) we could view surface topology and crystallinity of our epilayers. The layers appear to begin nucleating in islands. After some adjustments we came up with an Al flow rate that allowed us to grow $Mn_{0.56}Al_{0.44}$ epilayers which is precisely the target composition for τ-phase MnAl as reported in the literature. Again observing the surface topology with the AFM we were able to observe that the crystalline order was significantly improved with this 'recipe'. The deposition still appears to take place by nucleating in islands growing in the vertical direction more than would be optimal for uniform monolayer deposition. This needs to be confirmed with other analysis techniques.
5. The AFM analysis does indicate, however, that we have the ability to grow quantum dots of MnAl which are (so far) on the order of 1-2 nm thick and 30-50 nm in diameter. We believe that this opens a new potentially exciting opportunity to observe GMR in MnAl/GaAs nanocomposites at temperatures much higher than those of ErAs/GaAs systems. These results along with the Schottky barrier results constitute Ph. D. Dissertation by Brian T. Hemmelman defended in 1998 at SDSM&T.

4 Collaborations

We established a very productive collaboration with two prominent experimental groups: Prof. C. J. Palmstrøm's at the University of Minnesota (materials growth) and Prof. S. J. Allen's at the University of California at Santa Barbara (device properties and characterization); and with the theoretical group of Profs. W. Lambrecht and B. Segall at Case Western Reserve University (electronic structure of materials). As a result, we discovered *new fundamental aspects of spin-dependent transport in magnetic nanocomposites and heterostructures* concerning:

- the nature of *spin-dependent resonant tunneling* in ErAs/GaAs quantum wells;
- the mechanism of *colossal magnetoresistance* in ErAs/GaAs nanocomposites.

We also determined the nature of the Schottky barrier formation at the ErAs/GaAs interface and demonstrated MOCVD growth of MnAl quantum dots on GaAs substrate (see refs in the Appendix).

We will maintain close contacts with S. J. Allen's research group at the University of California at Santa Barbara and with C. J. Palmstrøm's group at the University of Minnesota. This work will focus on the theoretical support of their ongoing experimental studies of semiconductor-based magnetic heterostructures, nanocomposites, and isolated quantum dots.

5 Scientific Impact

We believe that our achievements may greatly facilitate several crucial areas of materials science and physics of semiconductor devices such as:

- physics of magneto-electronic materials,
- physics of non-coherent (hopping) conductivity in self-assembled arrays of magnetic quantum dots;
- physics of spin-dependent transport in magnetic heterostructures and quantum wells,
- magneto-optics and optically induced magnetism in magnetic semiconductor heterostructures.

This, in turn, will affect several device oriented areas of applied physics. For example, the recently discovered GMR effect is currently being used as a storage mechanism for digital information. It will permit storage densities far beyond those projected for silicon memories. These magnetic elements are non-volatile, that is they retain their memory state even when power is removed. Spin-dependent resonant tunneling diodes can be developed to the point that they will be suited for high-speed digital circuits operating at hundreds of GHz. It would be very attractive to add magnetic functionality to these ultra-fast devices by using magnetic semiconductors as their components.

6 Summary of New Findings

- First-principle electronic structure of technologically important bulk rare-earth compounds such as ErAs, ErN, ErP, GdAs, GdP, and GdN; first-principle analysis of the Shubnikov-deHaas spectrum of the ErAs layers burried in GaAs.
- First-principle electronic structure of technologically important bulk Mn alloys such as MnAl, and MnGa.
- First-principle electronic structure, total energies, and Schottky barriers of different ErAs/GaAs interfaces.
- Theory of spin-dependent interband resonant tunneling in GaAs/AlAs/ErAs resonant tunneling diodes. This may lead to a fabrication of novel semiconductor devices such as resonant tunneling spin-valves.

- Theory of giant magnetoresistance (GMR) of ErAs quantum dots immersed in GaAs matrix. This has a great potential for developing new non-volatile magnetic memory elements based on GMR.
- Epitaxial growth of MnAl layers burried in GaAs and demonstration of MnAl quantum dots' growth. We believe this opens a new opportunity to observe GMR in MnAl/GaAs nanocomposites at temperatures much higher than those of ErAs/GaAs systems.
- Numerical modeling of $Ga_xMn_{1-x}As$-based resonant tunneling diode (i.e. transmission coefficients, $I-V$-characteristics, spin polarization).

7 Future Plans

- Magnetooptical effects (giant Faraday rotation) in GaMnAs/GaAs heterostructures
- Giant magnetoresistance in all-semiconductor (GaAs/GaMnAs) magnetic multilayers
- Experimental study of magnetotransport in MnAl/GaAs nanocomposites
- Further theoretical studies of giant hopping magnetoresistance in magnetic nanostructures
- Further theoretical studies of spin-dependent resonant tunneling which include magnetic quantum dots in the Coulomb blockade regime

8 Personnel Supported

- Faculty: Andre Petukhov, Larry Meiners, Michael Foygel.
- Graduate Students: Brian Hemmelman, Denis Demchenko, Athanasios Chantis, Heather Ferguson, James Niggemann

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9 Publications & Presentations Acknowledging AFOSR Funding

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